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THE REVIVAL OF A FAILED CONSTRUCTED WETLAND TREATING A HIGH FE LOAD AMD

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1. ABSTRACT

Acid mine drainage (AMD) from abandoned mines has significantly impaired water quality in eastern Kentucky. A small surface flow wetland constructed in 1989 to reduce AMD effects and subsequently failed after six months of operation was renovated by incorporating anoxic limestone drains (ALDs) and anaerobic subsurface drains promoting vertical flow through successive alkalinity producing (SAPS) limestone organic compost beds. Two years of post renovation monitoring indicate that mean iron concentrations have decreased from 787 to 39 mg L^{-1}, pH increased from 3.38 to 6.46 and acidity has been reduced from 2,244 to 199 mg L^{-1}, ($CaCO_3$ equivalent). Mass removal rates averaged 98% for Al, 95% for Fe, 94% for acidity, 55% for sulfate and 49% for Mn during the study period. The combination of ALDs and SAPS technologies used in the renovation and the sequence in which they were implemented within the wetland system appeared to provide sufficient buffering and longer residence time rendering a promising design for treatment of this and other sources of high metal load AMD.

Characterization of sediments from abiotic/aerobic zones within the treatment system showed low SO_4/Fe ratios in initial abiotic treatment basins, supporting the formation of jarosite and goethite. As the ratios increased due to treatment and subsequent reductions in iron concentration, jarosite was transformed to other Fe-oxyhydroxysulfates and goethite formation was inhibited. Amorphous iron minerals such as ferrihydrite and $Fe(OH)_3$ were dominant in biotic wetland cell substrates. However, low Fe'+ activity, redox potential, and oxygen diffusion rates in the anaerobic subsurface environment inhibited crystalline iron precipitation. The formation of gypsum, rhodochrosite, and siderite as byproducts of alkalinity-generating reactions in this system also appeared to have an impact on S, Mn, and Fe solubility controls. Sustaining alkaline conditions within the wetland was necessary for maintaining metal retention consistency and long-term treatment efficiency.

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2. INTRODUCTION

The exposure and oxidation of iron sulfide materials as a consequence of coal mining activities has resulted in acid mine drainage (AMD), a serious water pollution problem for the Appalachian region. Acid mine drainage, a low pH, iron and sulfate rich water with high acidity is formed upon exposure of pyrite to the atmosphere. **Pyrite** (FeS_2), the most common sulfide in the bituminous coal fields, undergoes oxidation to form a variety of soluble iron sulfates which hydrolyze and produce AMD. As AMD enters natural waters, chemical and biological processes aid in the oxidation of iron from ferrous (Fe^{2+}) to the ferric (Fe^{3+}) state and the formation of ferric hydroxide precipitates commonly referred to as "yellow boy". The accumulation of ferric hydroxide precipitates on stream bottoms results in the formation of sediment layers which smother biological activity and contribute to further surface and groundwater contamination. The U.S. Bureau of Mines has estimated that approximately 20,000 km of streams and rivers are impacted by AMD in the United States and nearly 90% of these streams receive AMD from abandoned surface and deep mines.[1,2]

The Surface Mine Control and Reclamation Act (SMACRA) of 1977 and the Clean Water Act of 1972 require coal mine operators to meet established state or federal AMD discharge water quality standards. Current standards for active mines require a pH of 6.0-9.0, average monthly total Fe of 3.5 mg L^{-1}, and average monthly total Mn of 2.0 mg L^{-1} (Code of Federal Regulations, 1996). Conventional practices for the treatment of AMD requires the addition of highly alkaline chemicals such as sodium hydroxide ($NaOH$), calcium hydroxide ($Ca(OH)_2$), calcium oxide (CaO), sodium carbonate (Na_2CO_3), or ammonia (NH_3).[3,4] These reagents efficiently promote metal removal (via precipitation) and acidity neutralization; however, this type of chemical treatment can be very expensive and potentially dangerous to both humans and the environment when handled improperly.[5] In addition, chemical treatment is a long-term endeavor which requires continual support for reagents, labor and maintenance.

In recent years, however, several low-cost passive treatment technologies have been developed that utilize natural chemical and biological processes to clean contaminated mine waters without the burdens of chemical addition. Constructed wetlands, anoxic limestone drains (ALD), and successive alkalinity producing systems (SAPS) are some of the most progressive technologies that offer a potential solution to the AMD problem. The use of constructed wetlands is a viable alternative because they are not subject to the regulations and federal entanglements of natural waters and, therefore, provide ample opportunities for research and development of these man-made treatment systems. Since their inception, over 400 wetlands treating AMD from active and abandoned mines have been constructed in the bituminous coal region of the U.S.[6]

The types of constructed wetlands for AMD treatment are usually divided into two general categories: 1) surface flow or "aerobic" wetlands in which water Aows through emergent vegetation and above the surface of a relatively shallow sediment layer composed of clay on *in situ* soil, and 2) subsurface flow or "anaerobic" wetlands in which water flows through a relatively deep permeable sediment forcing the contact of drainage with plant roots and substrate materials. Substrates in "anaerobic" systems may be comprised of soil, peat moss, spent mushroom compost, sawdust, hay/manure compost, hay/straw bales, limestone and gravel, either alone or in various combinations. In general, aerobic wetlands treat AMD by promoting metal precipitation through oxidation/hydrolysis reactions and retention of the precipitate by physical entrapment. However, successful treatment by these systems is dependent upon initial pH and metal concentration.[7] Even though iron is removed from solution by hydrolysis, protons produced during the reaction may lower pH to levels suitable for causing plant stress or even death and resolubilization of retained metals.'

Most aerobic wetlands do not produce adequate alkalinity to buffer the acidity produced from hydrolysis, thus treatment of net acidic and moderate (20–75 mg L^{-1} Fe) to high (>75 mg L^{-1} Fe) metal content AMD by these systems alone has not been very successful.[7,9] Anaerobic wetlands also rely on oxidation/hydrolysis reactions near the surface, but primarily depend on chemical and microbial reduction processes within the substrate. Anoxic conditions, generated in the organic substrate are favorable for the formation of metal sulfides and alkalinity from bacterially mediated sulfate reduction (McIntire and Edenborn[10]). Bicarbonate production from limestone dissolution also acts as a buffer to neutralize proton acidity released from metal hydrolysis.[5,10]

Although limestone is the most inexpensive alkaline source in coal mining regions, it has been rarely utilized for AMD treatment because of its low solubility, and its tendency to become armored with ferric hydroxides in oxidized environments.[4,5,11] Turner and McCoy[12] discovered that buried beds of limestone, now referred to as anoxic limestone drains (ALD), can be useful in AMD treatment. In an anaerobic environment, ALD can raise pH to circumneutral levels and produce bicarbonate alkalinity without inducing precipitation of metal hydroxides and associated armoring. The alkaline water generated in the ALD builds up enough buffering capacity so that when it is exposed to aerobic conditions it can withstand hydrolysis and precipitation processes without dropping the pH level significantly.[13]

Recently, several systems have been developed which utilize both ALD and anaerobic wetlands processes. Kepler and McCleary[14] developed a successive alkalinity-producing system (SAPS) which promotes vertical flow of AMD through organic substrates and limestone beds. High biological oxygen demarid in the organic substrate promotes sulfate reduction and reduces iron to its ferrous state before entry into a limestone layer, which functions as a submerged ALD. Although the limestone layer does not represent a closed system, CO_2 levels increase under waterlogged conditions and facilitate the dissolution process: This system has the potential to neutralize large amounts of acidity and decrease treatment area requirements.

Even though the AMD constructed wetland technology has evolved considerably over the last two decades, the biggest successes came only recently when a serious attempt was made to rely more on the processes and mechanisms involved in the treatment rather than the trial and error approach of the early years. A substantial volume of knowledge is yet to be added to shed light into the complexity of these processes, but some of the recent findings of the "black box" chemistry have contributed to significant improvements in the wetland design parameters.

Constructed wetlands contain environments with alternating abiotic/biotic substrates, with a variety of pH and redox conditions, which influence solubility controlling processes and interactions between chemical species that may result in several alternative mineral formation sequences. Lazaroff et al.[15] reported that low pH AMD precipitates formed under abiotic conditions contained goethite with small amounts of amorphous hydrated Fe(III) sulfates and possibly jarosite, while those formed under biotic conditions and in the presence of *Thiobacillus ferroxidans* were dominated by amorphous hydrated Fe(III)-sulfates. Alternatively, the presence of organics and precipitated Fe-oxyhydroxysulfates in anaerobic environments appears to inhibit the formation of jarosite and may interfere with iron oxide precipitation through complexation.[16] The complexation of Fe with organic compounds lowers the activity of inorganic Fe(III) ions in solution, so that the solubility product of goethite is exceeded but not that of ferrihydrite. Since ferrihydrite is a precursor to the formation of hematite, the precipitation of hematite in an area with high organic matter content will also be inhibited. Thus, the prediction of metal removal scenarios in AMD constructed wetlands is complicated by an elaborate system of numerous physicchemical and redox reactions and interactions.

Although the general mineralogy of precipitates forming in AMD systems have been technically referred to as "amorphous" ferric hydroxides,[17] recent detailed studies have revealed many discrete minerals associated with AMD. which may have significant implications toward understanding metal attenuation processes in these extreme environments. Minerals such as ferrihydrite ($5Fe_2O_3\cdot 9H_2O$),[18] feroxyhite (δ-FeOOH),[19] jarosite ($KFe_3(OH)_6(SO_4)_2$)[20] and/or goethite (α-FeOOH)[21,22] are commonly associated with AMD precipitates Nordstrom" Suggested that "amorphous" ferric hydroxides found in AMD with $pH < 3.5$ may consist of jarosite transforming to ferrihydrite or goethite upon dilution. However, Bigham *et al.*[23] found that the "amorphous" ferric hydroxide associated with AMD of pH 3.0–4.5 is a poorly crystalline Fe-oxyhydroxysulfate called schwertmannite. Schwertmannite has a structure similar to that of akaganeite (β-FeOOH) and is distinguished from it by a sulfate content averaging 12 to 16% by weight and an Fe/S ratio in the range of 5.3 to 8.[23] Bigham *et al.*[24] also suggested that ferrihydrite is a product of rapid hydrolysis of Fe(III) and dominates at $pH > 5$, white goethite is a tract compound of AMD sediments resulting from alterations of other mineral phases and possible interactions with carbonates,

The formation of precipitates within the drain poses the greatest problem in limiting ALD efficiency. The solubility of hydroxides decreases with an increase of pH; thus, precipitation of ferric hydroxide at pH 3 to 4 (especially if the drain is not entirely anoxic) and aluminum hydroxide at pH 4 to 5 may occur as limestone dissolves.[25] Bicarbonate production from the dissolution may also react with Fe^{2+} and Mn" to form siderite ($FeCO_3$) and rhodocrocite ($MnCO_3$). In moderate to high metal content AMD, alkalinity release may be controlled by the solubility of $FeCO_3$ or $MnCO_3$, if present, which have lower solubility and alkalinity generation rates than $CaCO_3$.[26] In addition, calcium released during limestone dissolution is capable of forming gypsum ($CaSO_4$) within the drain, especially in systems with long retention times' Physical characteristics of precipitates within the drain may differ (form amorphous gels) from those found in highly oxidized environments; hence, removal of substances clogging the drain could possible be performed by agitation or flushing.

In the relatively short history of application of the constructed wetland technology for AMD treatment, there have been successes and failures While design improvements have contributed to greater efficiency of newly constructed systems, some of the old systems experienced failure or unsatisfactory performance due to design flaws or extremely high AMD loads Most of these flawed systems are abandoned or buried and/or replaced by new systems. This paper presents a case study in which a failed constructed wetland treating a highly toxic AMD was completely overhauled in its original position and produced a functioning system which was more effective than the original.

3. MATERIALS AND METHODS

3.1. The Jones Branch Constructed Wetland

Underground coal mining in the Rock Creek watershed began in the early 1900's and continued until the mid 1960's. The Steams number 2 coal seam and overlying geologic strata found in this area contain high sulfur and pyrite quantities which generate low pH and high metal content AMD. Jones Branch, a tributary of White Oak Creek, joins Rock Creek and eventually flows to the Big South Fork of the Cumberland River in McCreary Co. Kentucky (36°42.64 N, 84°36.92 W) (Fig. 1). Acid mine drainage from several abandoned underground mines and approximately six hectares of pyritic coal waste piles has degraded the water quality and impaired the aquatic biota of the creek.[27] In an effort to restore water quality, a constructed wetland was designed to receive and ameliorate AMD from two collapsed portals to a 91 hectare mine located approximately 2.25 stream kilometers above the confluence of Jones Branch and White Oak Creek. The U.S. Forest Service's Daniel Boone National Forest supervised construction of the wetland and access road to the site during the summer of 1989.

The original wetland designed at Jones Branch consisted of two sequential ponds with 15 and 10 cells, respectively, providing 1,022 m^2 of treatment area. Each cell consisted of 23 cm crushed limestone over a compacted floor treated with bentonite clay. A 46cm layer of spent mushroom compost was placed over the limestone to serve as an organic substrate. The substrate was topped with 19 kg per 100 m^3 hydrated lime, 3.4 kg of superphosphate, and a 4.5 kg of IO-IO-IO fertilizer. Cattails (*Typha latifolia*) were transplanted in the substrate on a three foot center pattern and gradually introduced to the AMD.

From the mine seeps, AMD was collected in a settling basin, then Burned into the first wetland field, where it flowed in a serpentine fashion through fifteen ceils to a second flume that led to the second wetland field. After flowing through ten cells in the second field, treated water exited the wetland and flowed into Jones Branch. The design provided approximately 14 to 46 m^2 of surface area per liter inflow per minute at a flow rate of 200 to 100 L/min, respectively. The surface flow orientation of the wetland allowed for a flow path of 200 linear meters. which resulted in a residence time of approximately two hours H-flumes at the settling basin and at the outlet of each wetland field were used to monitor flow. Post-construction monitoring and chemical analyses were performed by the Northeastern Forest Experimental Station from June, 1989 to June, 1992.

The initial AMD had an average pH of 3.0. 1,250 mg/L Fe, 21.5 mg/L Mn. 18 mg/L Al, and 4,000 mg/L SO_4^{2-} (Ref. 28). Metal concentrations and acidity were reduced substantially during the first six months of treatment, however, the system failed thereafter due to insufficient utilization of treatment area, inadequate alkalinity production and metal overloading.

3.2. Wetland Renovation Design Criteria

In an attempt to revive the treatment system, a two phase renovation project began in 1995 that incorporated the use of anoxic limestone drains and a series of anaerobic subsurface drains to promote vertical flow through limestone beds overlain by organic compost (Fig. 2).

Limitations in the topography of the site prevented expansion. So design modifi-

Figure 1. Location of the Jones Branch wetland: McCreary County, Kentucky.

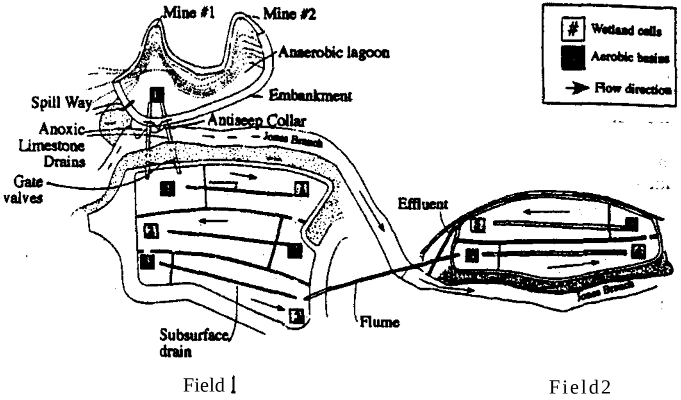

Figure 2. Sight plan and sample locations for the Jones Branch wetland.

cations were selected that could maximize available surface area. increase retention time. regulate flow and facilitate alkalinity production. Drainage from the mine seeps contained low dissolved oxygen (<1.0 mg/L) and ferric iron (<25 mg/L) concentrations which made it suitable for ALD treatment. However, the steep mountainous terrain and the presence of a creek through the site prevented excavation of the traditional trench to install the ALD system. Instead, large PVC pipes filled with limestone and equipped with flow control gate valves were expanded across the creek and into the existing wetland. Both ends of each drain were maintained submerged to sustain anoxic conditions within the pipes.

A modified SAPS design was also applied to force more interaction of AMD with the substrate (limestone/compost) and enhance alkalinity production processes and greater retention of drainage within the system. Aerobic precipitation basins followed each subsurface wetland to promote hydrolysis and metal precipitation (Fig. 2). This compost substrate was chosen for its characteristically high permeability, low cost (transport) and capacity to remove metals from AMD.[29] Cattails (*Typha latifolia*) were selected as the vegetation species for their tolerance to high acidity and metal content, and ability to transport oxygen via their aerenchyma tissue from the atmosphere through the plant root and into the adjacent substrate.[30] Mixing of substrate components was encouraged during placement to readily reduce any ferric iron that enters the drainpipes.

The treatment principle of the new design was to generate enough alkalinity in the ALD's and anaerobic wetland cells to promote metal precipitation while compensating for acidity produced during hydrolysis in aerobic zones. With each subsequent treatment series, the amount of alkalinity produced is expected to increase as the concentration of metals decreases, so that the final effluent is net alkaline. In addition, the system was also expected to provide supplementary treatment through organic complexation of metals adsorption to exchange sites, physical entrapment of solids. uptake by plants, and precipitation of metal carbonates.

3.3. Wetland Renovation Plan Implementation

The renovation project for the Jones Branch Wetland began in May, 1995. The renovation stages involved: removal of preexisting substrate: installation of anoxic limestone drains: converting the original surface flow system with a modified SAPS” design; and addition of a new substrate. The original organic compost was excavated from the wetland, taken to a refuse area and deposited over 15 cm graded limestone. Armoring in the original wetland limestone substrate was not evident and efforts were made to reuse as much as possible. An anaerobic lagoon was constructed by creating a berm that surrounded the portals and pooled AMD from the seeps The berm was approximately two meters high and was lined with a high density polyethylene sheet. The lagoon was equipped with an emergency spillway for periods of high flow or malfunction of the ALD's. After completion, Floating bags filled with compost were placed in the lagoon to reduce surface aeration and oxidation of Fe^{2+}.

Anaerobic AMD 5 feet below the surface of the lagoon was diverted to the wetland through two PVC pipes 0.5 meter in diameter and 12.2 meters in length. The pipes were filled with #4 (2.5–7.5 cm) crushed limestone and wrapped with pipe installation. The inlets of the drains were covered with screening caps to keep large debris from entering the ALD's. A 30cm gate valve installed at the outlet of each ALD regulates flow through the drain and into the 1,022 m^2 wetland. The gate valves are also used to control the quantity of water within the anaerobic lagoon.

In the wetland fields, AMD flows through a series of five alternating abiotic/biotic treatment zones (Fig. 2). AMD collected in a precipitation basin with no organic substrate or plants flows into the subsurface of a wetland cell through a perforated 15 cm diameter PVC pipe. The AMD percolates through holes in the pipe into a substrate, composed of 30cm of crushed limestone (≈350 tons) overlain by 50 cm of hay/manure compost planted with cattails. Drainage flows through three treatment zones in the first field and proceeds through a flume into the second field and two more treatment zones before being discharged into Jones Branch. H-flumes at the outlet of each wetland field are used to measure flow.

Pre-renovation monitoring of the wetland system began in July of 1994. Construction of the anaerobic lagoon, anoxic limestone drains and renovation of wetland field (Phase I) began in May 1995 and was completed in June 1995. Renovation of wetland field 2 (Phase II) began and was completed during the last week of September 1995.

3.4. Sample Collection

Water samples were taken after renovation on a bimonthly basis from June, 1995 through the end of October 1996. Nine water sampling stations were located within the project site. including the mine seep, anaerobic lagoon; precipitation basins I, 2. 3, 4 and 5; and wetland cells 3 and 5 (Fig. 2). Three water samples were collected at each station. One sample was preserved with HNO_3 to $pH < 2.0$ for total iron, manganese. magnesium and calcium analyses. A second sample was preserved with $2N$ zinc acetate and NaOH to $pH > 9$ for sulfide analysis. The third sample was used as sampled for the determination of acidity, alkalinity, sulfate, aluminum, total suspended solids, total solids and ferrous iron. Water pH, dissolved oxygen, conductivity, temperature and redox potential were measured *in* at each sampling station. Samples were transported with ice in coolers and stored at 4°C prior to analysis.

Sediment samples were collected at each wetland cell and precipitation basin. The sediment samples were composites representing the entire 50 cm depth of the organic substrate in wetland cells, and the upper 5 to 10 cm depth of the precipitation basins. In addition. another set of samples was collected which differentiates the upper 25 cm and lower 25 cm depths of the organic compost layer. Interstitial solutions were extracted from the sediments within 24 hours of collection by centrifugation (3,000 rpm for one hour), filtered through 0.2 mm filters, and immediately analyzed for pH, conductivity and redox potential.

3.5. Solution Analysis and Sediment Characterization

Surface waters and extracted interstitial solutions were analyzed for total Fe, Mn, Mg and Ca using a IL S 11 atomic absorption spectrophotometer. Aluminum was determined colorimetrically by the eriochrome cyanine-R method and measured with a Bio-Tek Instruments spectrophotometer microplate autoreader. Acidity and alkalinity were measured by titrimetric procedures using a Metrohm 665 Dosimat. Sulfate was determined turbidimetrically using the barium chloride method. All sample handling and solution characterization procedures followed those outlined in the Standard Methods for the Examination of Water and Wastewater, APHA.” Geochemical modeling of aqueous-phase chemical equilibria was performed with the MINTEQA2 computer program.[32] Measured pH and Eh values ware used as model inputs in the computer simulation.

A set of sediment samples, collected one year after the renovation, was sequentially extracted to determine the exchangeable, organically bound, poorly crystalline, crystalline and residual forms of metals bound to the substrate. Untreated sediment samples were analyzed for organic carbon content with a Leco CR12 carbon analyzer. Mineralogical characterizations were performed with a Phillips PW 1840 diffractometer and PW 1729 X-ray generator. A Dupont 951 thermal analyzer was used for thermogravimetric (TG) and diffenntial thermogravimetric (DTG) analysis

4. RESULTS AND DISCUSSION

4.1. Pre-renovation Water Quality

Influent water quality data from the Jones Branch wetland showed much higher acidity, iron and sulfate, but slightly lower manganese and aluminum concentrations than average levels observed in other AMD treatment wetlands throughout the eastern U.S. The original wetland design proved to be sufficient at reducing metal levels and acidity during the first six months of operation, but failed thereafter (Table I). Average pH levels rose from an influent level of 3.05 to 7.20 in the effluent during the first year. however, effluent pH levels consistently remained below influent levels in subsequent years Apparently, hydrated lime which was topdressed on the substrate efficiently promoted metal precipitation and buffered the initial acidity produced during metal hydrolysis, but neutralization ceased as the carbonate source was exhausted.

The initially elevated pH levels decreased the solubility of metal hydroxides and led to >95% reductions in iron and aluminum. Manganese and sulfate levels were also reduced by ≈80% during this period. However, increased acidity in subsequent years curtailed metal hydroxide precipitation of Mn and Al. Inhibition of microbial processes

Table 1. Comparison of inflow and outflow water quality data prior to renovation at the Jones Branch wetland.†

Influent

Date‡	n*	pH			Fe			Mn			Al			SO_4		
		Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
1989	8	2.89	3.05	3.33	960	1256	1420	15.8	22.2	37.3	8.1	12.4	20.6	3490	4311	5290
1990	10	2.83	3.19	3.61	560	937	1218	10.4	17.3	22.8	6.8	10.4	14.3	2700	3725	4600
1991	11	2.94	3.15	3.69	475	1017	1322	8.5	19.1	47.0	3.9	17.2	38.8	2000	3655	4800
1992	9	2.68	3.30	3.85	888	1229	1440	16.3	18.1	20.2	25.4	35.9	42.8	4100	4363	4600
94/95	5	3.24	3.47	3.87	225	739	1149	4.2	8.4	16.6	9.1	15.0	26.7	1098	2559	5385

Effluent

Date‡	n*	pH			Fe			Mn			Al			SO_4		
		Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
1989	8	6.10	7.20	7.92	0.11	336	231	0.29	4.18	13.7	0.2	0.5	0.7	12.0	763	2460
1990	10	2.49	2.98	5.33	145	452	768	7.7	14.4	20.3	0.5	8.2	12.3	1550	3028	3800
1991	11	2.48	2.59	2.77	223	467	856	7.8	15.8	38.8	4.1	12.0	25.9	1650	2661	3900
1992	9	2.74	2.79	2.82	558	848	1038	13.1	15.4	17.8	26.5	33.8	39.7	3100	3880	4500
94/95	5	2.37	2.53	2.72	193	452	755	6.1	9.3	19.4	4.0	44.5	18.5	1572	2665	5010

†Values in mg L^{-1} except for pH which is in standard units.
‡Analysis from 1989-1992 performed by U.S. Forest Service Northeastern Experimental Station.
*n = number of samples.

due to high acidity and armoring of some limestone within the substrate probably contributed to the lack of alkalinity generation. Under these low pH conditions, resolubilization of previously retained metals could have acted as a secondary source of water contamination.”

Several studies[33,34] have suggested that adsorption and complexation of metals in organic substrates occurs only in the initial few months of AMD exposure before becoming saturated. During the 1990-1992 period, a reduction of only ≈20% Mn and Al occurred, which indicates that many of the metal retention processes had ceased. With more aging, Mn levels in the effluent exceeded those of the influent. Apparently, the wetland substrate had become saturated with accumulated metals leading to resolubilization of precipitated Mn. In addition, reduction of sulfate declined with each passing year, indicating lowered microorganism metabolism rates or inadequate infiltration and retention of AMD within the substrate zone.[10] A -30% reduction in iron concentration continued from 1990 through 1995. evident by low pH levels in effluent waters and the accumulation of ≈10cm layer of yellowboy above the substrate. Water quality parameters had significantly deteriorated by 1995. so that effluent water quality was equal to or worse than water coming into the system. Aesthetic qualities had also deteriorated and suggested failure of the system through mass vegetation die-off and precipitate accumulation throughout.

4.2. Post Renovation Water Quality

With the completion of Phase I renovation, influent pH levels rose from 3.1 to 6.4 at the flume, then dropped to 5.3 in field 2. This trend remained constant until Phase II renovation was completed, suggesting that the old substrate was acting as a source of contaminants to the Phase I partially treated mine water. Effluent pH levels increased to 6.5 and remained higher than flume pH levels for all sampling events that occurred after Phase II had been completed (Fig. 3a).

The pH of the water within the wetland is very important because it influences the solubility of metal hydroxide precipitates: the kinetics of metal oxidation and hydrolysis; and the viability of iron catalyzing the sulfate reducing bacteria. Autooxidation of ferrous iron in abiotic systems predominates above pH 5,” while chemolithotrophic microbial iron oxidation occurs at lower pH levels (1-4). Aluminum hydrolysis occurs at pH ≈ 5,[17] and micmbially catalyzed Mn oxidation occurs at pH > 6.” Silver” also noted that a pH > 5 is necessary for sulfate reduction in AMD systems Therefore, reaching and maintaining a pH ≈ 6 in the treatment system is necessary for the adequate treatment of AMD and the prevention of secondary contaminations through metal resolubilization.

Post renovation influent and flume pH values remained relatively constant except for an increase that occurred during January 1996, which may have been caused by freezing conditions and ice formation within the system. Post renovation effluent pH values, however, showed a gradual increase from 5.3 to 7.6 during the first nine months followed by a drop to 6.4 where it stabilized for the rest of the study period. Flume and effluent pH values indicate favorable conditions for precipitation of metal hydroxides. The increased pH levels also suggest the production of a sufficient amount of alkalinity to neutralize the acidity produced from hydrolysis. The slight decline in pH during the last four months may indicate that some of the limestone neutralizing potential associated with the finer particles may have been exhausted and the buffering reached a steady state condition.

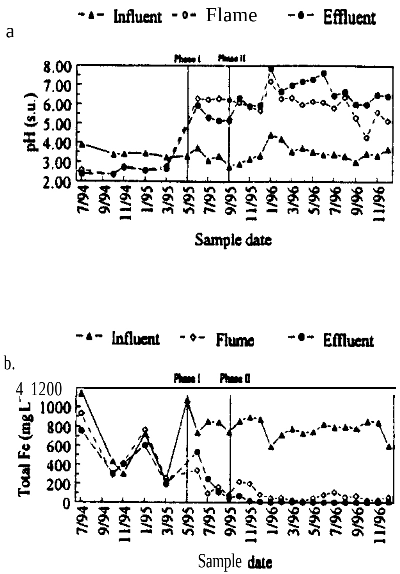

Figure 3. Wetland performance data for a) pH; b) total alkalinity; c) total iron; and d) aluminum at the influent, flume, and effluent sampling points.

Post renovation Eh values at the Jones Branch wetland suggested both oxidizing and reducing zones within the system (Table 2). Influent surface water samples displayed a moderately reduced redox potential (260 mv), which increased as drainage was exposed to oxygen in the first precipitation basin. In the biotic wetland cells, Eh values were greatly reduced due to low oxygen diffusion rates and high oxygen demand by the organic compost. However, the Eh increased again as the drainage left the wetland cell and moved into the next abiotic basin due to ample surface aeration and a decrease in the biochemical oxygen demand. In general, surface water samples displayed higher Eh levels than subsurface waters, and abiotic basins showed higher Eh values than biotic wetland cells. Therefore, metal speciation and solubility controls are expected to vary between these zones of differing oxidation.

A comparison of the post renovation Eh and pH values suggests that influent samples were operating under reduced conditions with soluble ferrous (Fe^{2+}) iron as the dominant iron species. Effluent samples, on the other hand, exhibited lower Eh values than influent waters, but the increase in pH probably shifted iron stability to the ferric (Fe”) form with insoluble $Fe(OH)_3$ as the dominant solubility control species. The relationship between Eh and iron redox chemistry is of great consequence to alkalinity production since $Fe(OH)_3$ has the capability of coating and armoring limestone, rendering it less effective or useless. Subsurface water samples collected from within the limestone substrate zone indicated higher pH and much lower Eh levels than surface waters. In the biotic wetland cell substrates Eh values ranged from 13.2 to -72.5, which implies highly reduced conditions and the prevalence of ferrous iron. Also, a submersible dissolved oxygen (DC) probe used at the inlet and outlet of the ALD's to evaluate redox conditions indicated DO levels lower than 2 mg L^{-1} throughout the post renovation period. Thus, the armoring of limestone should be prevented in both ALD and substrate environments based upon the prevailing redox conditions.

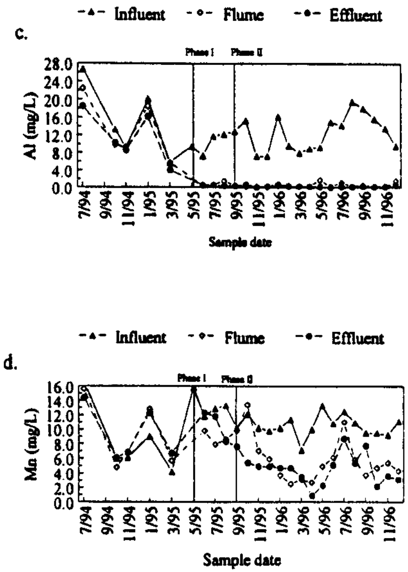

Figure 3. Continued

Pre-renovation samples at all locations and all influent samples throughout the study contained no titratable alkalinity and zero buffering capacity to combat acidity produced during hydrolysis of metals Immediately after the renovation. alkalinity levels at the flume displayed drastic increases to 1,268 mg $CaCO_3$ L^{-1}. Dissolution of limestone dust and fines accumulated in the system probably elicited this response. Alkalinity generation in flume samples was erratic with values ranging from zero to 238 mg $CaCO_3$ L^{-1} (Fig. 3b). Post renovation wetland effluent samples, on the other hand, displayed an increase from zero to ≈200 mg $CaCO_3$ L^{-1} during the first nine months, then fell to ≈100 mg $CaCO_3$ L^{-1} during the last few months of the study. Apparently, limestone dissolution peaked during the first nine months and moved toward a steady state afterward.

Table 2. Mean Eh and pH values from surface and subsurface water samples.[†]

	Surface wter									
	Lagoon	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
Eh (mv)	260.6	294.8	345.4	246.8	169.1	264.3			83.8		159.3
pH	3.38	3.20	3.19	4.62	5.69	4.83			6.07		6.46

	Subsurface water										
	Lagoon	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
Eh (mv)	269.12	176.6	67.84	-10.06	48.2	97.9	13.2	-14.3	6.7	-28.1	-72.5
pH	3.51	3.93	5.53	6.20	6.04	5.36	5.76	6.35	6.63	7.16	7.72

†Sample sites are indicated as, B# = abiotic basin; C# = biotic wetland cell.

Alternatively, this reduction may be an indication that some iron coating of limestone particles may be taking place in the substrate.

Post renovation analysis also displayed a drastic reduction in iron levels Mean influent total Fe levels dropped from 787 to 110 and 37 mg L^{-1} at the flume and effluent, respectively (Fig. 3c). This accounted for an 86% Fe reduction in field I and a total reduction of 95% for the entire system. Mean effluent Fe levels did not meet Office of Surface Mining discharge guidelines for the entire post renovation period, but samples from 11/95 through the end of the study period contained an average of 3.3 ± 2.5 mg L^{-1} Fe, which would satisfy the discharge criteria.

Iron retention in the wetland system was the result of several precipitation and/or adsorption processes at the surface and within the substrate as documented by sediment characterizations. The formation of insoluble oxyhydroxide, carbonate. and sulfide precipitates within AMD treating wetland systems have been suggested to be responsible for the observed reduction of iron in effluent samples The hydrolysis of ferric iron or microbial oxidation of ferrous iron usually accounts for 40 to 70% of the total iron removed from AMD by wetlands,[34] while nearly 30% of the iron retained may be an iron sulfide form.” Limestone dissolution and high pCO_2 concentrations in the wetland substrates may also provide the conditions necessary for iron carbonate precipitation.

Sequential extractions of substrate samples revealed that nearly 70% of the iron within the Jones Branch wetland was in the oxyhydroxide form. Sequential extractions also indicated the potential for crystalline iron sulfide precipitation, however, AMD samples indicated undersaturation with pyrite. The high pCO_2 levels expected within the limestone wetland substrates may also favor siderite precipitation. Therefore, the remaining ≈30% of iron retained in the wetland may be attributed to siderite precipitation, adsorption to exchange sites, and/or organic complexation. Even though the solution data suggest that pyrite formation is not favored under the current conditions, future precipitation with solution chemistry shifts is possible.

The fate of acidity corresponds almost identically to that of Fe. which implies that much of the acidity produced originates from the precipitated iron.[18] Moreover, iron oxidation and hydrolysis reactions are strongly influenced by the solution pH so that high levels of acidity may result in low metal removal rates. It has been shown that rate constants for the formation of iron precipitates increased from minutes and hours at circumneutral pH values, to months and years as pH falls below 4.[17] Therefore, the maintenance of high alkalinity levels is necessary for continued metal removal within the wetland system.

Aluminum concentrations were reduced by 98% through the wetland after renovation and low levels (<0.7 mg L^{-1}) were observed in the effluent throughout the post renovation period (Fig. 3d). This reduction may be attributed to the solubility of Al which is pH dependent and forms aluminum hydroxide precipitates at pH ≈ 5.0.” Interstitial solution analysis revealed that a pH of 5.76 was achieved in the subsurface of the first wetland cell and maintained at or above this level in subsequent substrate zones.

Manganese concentrations, on the other hand, displayed a moderate 48.6% reduction through the wetland system (Fig. 4a). Several researchers have reported low removal efficiency rates for Mn in wetland treatment systems,’ and attributed them to several biogeochemical interactions and slow kinetic processes of Mn^{2+} oxidation.” A pH of 8 to 10 is generally accepted as the level needed for uncatalyzed Mn oxide precipitation.” which, unfortunately, is infrequently reached in AMD treatment environments. Manganese oxide precipitation can occur at lower pH levels (6–8) by coprecipitation with Fe

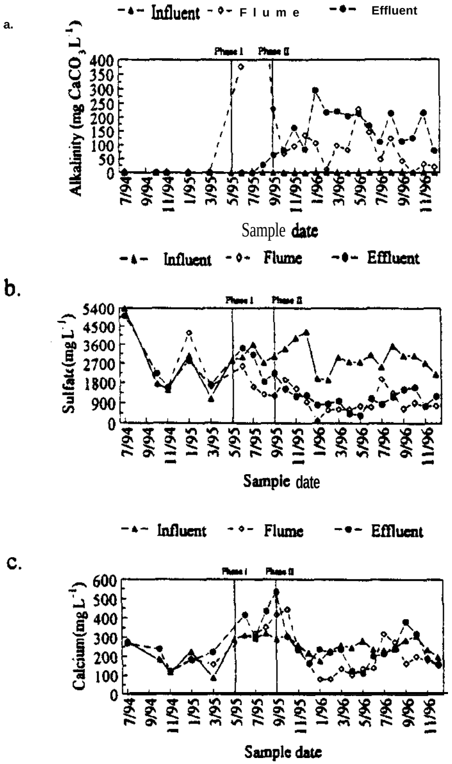

Figure 4. Wetland performance data for a) manganese; b) sulfate; and c) calcium at the influent, flume and effluent sampling points.

oxyhydroxides.[8] However, ferrous iron may control Mn oxidation rates in reduced environments by contributing electrons to previously precipitated Mn oxides and producing soluble Mn.$^{2+5}$ Manganese retention in the Jones Branch wetland appears to be influenced by all of these factors.

Flume and effluent Mn concentrations displayed an initial reduction from influent levels but with considerable fluctuation between 30 and 90%. This initial reduction of during the first few months after the renovation appears to be the result of sorption processes, as sorption sites on organic matter and limestone at that time were plentiful.“@ Sorption of Mn onto carboxyl and hydroxyl functional groups in fresh compost occurs upon exposure, but can soon become saturated. Sorption of Mn onto limestone may also occur by displacement of soluble Ca^{2+} for Mn^{2+} and formation of a solid phase $MnCO_3$ at the surface.”

The concentration of Mn in the flume and effluent, after November 1995, appears to be influenced by loading rates and Fe^{2+} concentrations. After Phase II renovation. flume and effluent Mn levels gradually dropped during the first eight months then incPreased in the following four months before falling again toward the end of the study (Fig. 4a). This trend was consistent with influent Mn loading rates of 3 18 ± 107 g day^{-1} and 645 ± 107 g day^{-1}, respectively. The analytical data also revealed a negative relationship between total Mn and Fe^{2+} in flume waters (r = -0.85). suggesting that oxidation was inhibited by the presence of ferrous iron within the system. This relationship can be used to explain the variable Mn treatment rates Areas displaying low Fe” concentrations exhibited high Mn retention. while high Fe*’ content corresponded with low Mn treatment efficiency.

The concentrations of SO_4^{2-} in the surface water decreased by 53.4% as it passed through the wetland, suggesting that sulfate reduction might be an active process (Fig, 4b). However, low S^{2-} concentrations (<5 mg L^{-1}) in surface and interstitial samples indicated that iron sulfide precipitates were not likely to form. According to Postgate,[41] sulfate reducing bacteria (SRB) am inhibited by SO_4^{2-} concentrations above 1,200 mg L^{-1} and redox potentials >100 mv. The SO_4^{2-} concentrations and oxygen levels observed during the post renovation period were above these levels and, therefore, not suitable for dissimilatory sulfate reduction. However, geochemical modeling suggested that conditions were favorable for the formation of gypsum ($CaSO_4$) in the interstitial solution samples and surface water samples from aerobic basins 3 and 5. Therefore, the observed decrease in sulfates can be explained by gypsum precipitation. Average surface water effluent SO_4^{2-} concentrations were higher than those observed in basins 3, 4, 5 and wetland cell 3. and interstitial solutions exhibited increased SO_4^{2-} retention with each successive treatment zone (Fig. 5). It is likely, that changes in the water quality promoted resolubilization of precipitated interstitial gypsum in the last wetland cell.

The fate of Ca^{2+} in the system is closely associated to that of SO_4^{2-}. Average surface water effluent Ca^{2+} concentrations were generally higher than those observed in the influent, however, flume Ca^{2+} levels were consistently lower than those observed in both influent and effluent (Fig. 4c). Interstitial Ca” levels exhibited a moderate 3 1% increase between the lagoon and aerobic basin 2, suggesting limestone dissolution (Fig. 5). In sub sequent treatment zones. the concentration of Ca^{2+} fell. possibly due to gypsum precipitation, then rose in the last wetland cell. Even though gypsum precipitation was favored throughout the treatment system in interstitial zones, the influence of oxygen in the upper water column may have had an impact on its stability.

4.3. Treatment Efficiency

Evaluations on the performance of AMD wetland treatment systems are often based on treatment efficiencies. where effluent concentrations am compared to influent concentrations. However, this approach is not very informative because the influence of flow rate on performance is withheld.[34] Therefore, loading rates representing the mass of a contaminant entering and leaving the wetland system as the product of its concentration and the hydraulic flow rate provide a better measure of treatment efficiency.

Average influent and effluent flow rates after renovation were 37.1 and 26.1 L min^{-1} respectively. The large difference in the values is attributable to evapotranspiration losses and a leak that was detected and sealed in April, 1996. After the leak was repaired, effluent flow rates varied less than 1.5 L min^{-1} from the influent rate. Prior to renovation, retention

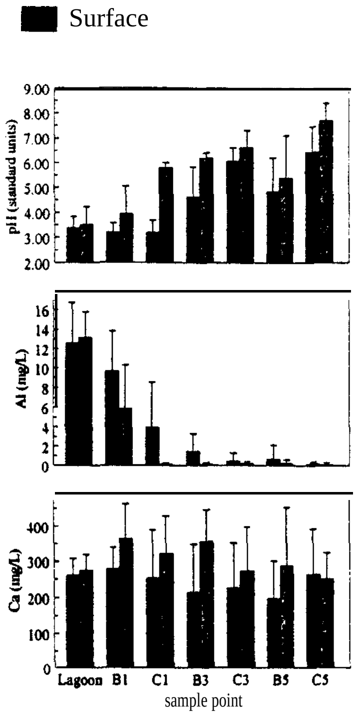

Figure 5. Mean surface water (n = 26) and interstitial solution (n = 6) chemistry for post renovation sampler B(#) = abiotic basic, C(#) = wetland cell, = standard error.

of drainage within the system was estimated to be ≈2 hours (Chalfant[28]). A tracer study similar to the one performed by Hellier[42] conducted to determine retention time in the renovated system showed an increased residence within the system to nearly three days.

Post renovation influent Fe loading rates ranged from 16.5 to 59.3 kg day^{-1}, and averaged 42.0 kg day^{-1}. Post renovation effluent Fe loading rates ranged from 10.5 to 0.03 kg day^{-1}, and averaged 1.4 kg day^{-1}. Based on these values, the wetland retained 18,676 kg (18.7 metric tons) of iron during the post renovation period. The average acidity load input was 120 kg day^{-1}, while output levels were reduced to 4.47 kg day^{-1}. Thus, 53,144 kg (53.1 metric tons) of acidity were neutralized during the post renovation Period. It was also estimated that the wetland retained an average of 0.37 kg Mn day^{-1}, or 170 kg of Mn over the entire study period.

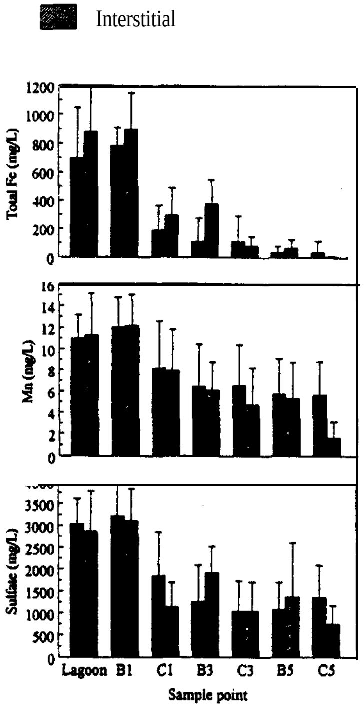

Figure 5. *Continued*

4.4. Mineral Solubility Controls

The changes in AMD composition at different locations within the wetland suggest that different solid phases may control the solution chemistry at different stages of treatment. Solution saturation indices (logQ/K), where Q = ion activity product and K = solubility product constant were calculated using the MINTEQA2 speciation program. Interstitial solutions and surface waters were found to be supersaturated with respect to hematite (αFe_2O_3) and magnetite (Fe_3O_4) throughout the wetland. Interstitial solutions were undersaturated, while surface waters were supersaturated with respect to jarosite. This is most likely due to the lack of sufficient Fe^{3+} in the substrate Interstitial solutions appeared to be near saturation with lepidocrocite, while surface waters were supersaturated. Interstitial solutions showed a gradually decreasing undersaturation with respect to ferrihydrite, while surface waters became supersaturated with progressive treatment.

Gypsum ($CaSO_4$) and jurbanite ($Al(OH)SO_4$) appeared to be at or near saturation in all surface and interstitial solution locations. Minerals containing aluminum such as basaluminite ($Al_4(OH)_{10}SO_4$) and boehmite (γ-AlOOH) displayed undersaturation in the lagoon and first precipitation basin with supersaturation in all other sample locations of the interstitial solutions. Iron sulfide species maintained low (c-30) saturation indices at all surface and interstitial locations.

The mineral stability diagram (Fig. 6) depicts the solubility lines of goethite, lepidocrocite, amorphous $Fe(OH)_3$, and ferrihydrite with solubility product constants (pFe^{3+} - 3pH) of 0.02, -1.39, -3.5 and -5.0 respectively.[43,44] and an average pSO_4^{2-} of 2.25 representative of the solutions studied. The jarosite line is plotted for $pK = pK^+ + 3pFe^{3+} + 2pSO_4^{2-} = 12$,[44] and $pK^+ = 3.3$. In this diagram, a point lying below a solubility line is supersaturated with respect to that mineral while one above the line is undersaturated. Points to the left of the solubility line for gypsum are supersaturated with respect to the mineral, while those to the right are undersaturated.

From the diagram, it is obvious that interstitial solutions and surface waters are controlled by different processes. A possible Fe controlling sequence for interstitial solutions could include goethite in the lagoon and first precipitation basin, lepidocrocite and amorphous $Fe(OH)_3$ for the remaining precipitation basins and the first three wetland cells, and amorphous $Fe(OH)_3$ and ferrihydrite for wetland cells 4 and 5. This sequence supports data from dissolution analyses and confirms the relationship established by Schwertmann *et al.*[21] for $Fe_{(ox)}/Fe_{(CBD)}$ vs. organic carbon. Surface water samples, however, fluctuate between the solubility of amorphous $Fe(OH)_3$ and ferrihydrite in initial abiotic sites, while subsequent abiotic and biotic sites are supersaturated with respect to all Fe oxide and hydroxide minerals included. Points from both surface and interstitial solutions display individual regression lines that are parallel to jarosite suggesting possible control of Fe’+ by an iron sulfate mineral.

Iron oxyhydroxysulfates with variable Fe/S molar ratios (3.5–5.0) were suggested as a possible solubility controlling species akin to jarosite which exhibits a Fe/S ratio of 1.5.[15] The Fe/S molar ratios of sediment samples in this study, corrected for contribution of non-sulfate bearing minerals and gypsum, were between 3.1 and 6.1 for abiotic sampler These ratios are consistent with those reported by Bigham et *al.*,[23] and Karathanasis and Thompson,[16] and can he described ‘by the chemical formula $Fe_{16}O_{16}(OH)_{10}(SO_4)_3$ with Fe/S of 5.3. Surface waters with low Fe^{3+} activity are clustered around the Fe-oxyhydroxysulfate solubility line created for the previous formula with a Fe/S ratio of 5.3 (Fig 6). Based on this formula, Fe solubility control of both abiotic and biotic surface water samples should include Fe-oxyhydroxysulfates and ferrihydrite at low Fe^{3+} activities and Fe-oxyhydroxysulfates and jarosite at higher Fe? activities The Fe/S ratio of biotic wetland cells is similar to that of jarosite (1.3–2.0), which suggests S-enrichment of the substrate. However, biotic sediments remain undersaturated with respect to jarosite even at points where the Fe/S ration is ≥ 1.5. Apparently, low Fe” activities and low oxygen diffusion rates in the subsurface inhibit the kinetics of jarosite pmcipitation. The stability diagram also indicates that several points at later stages of treatment may be in equilibrium with gypsum, which may influence SO_4^{2-} activity and prevent jarosite formation.

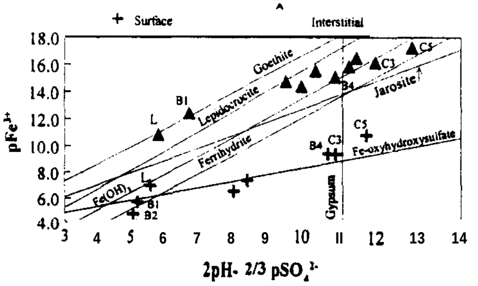

Figure 6 . Mineral stability diagram depicting solubility lines o f goethite, lepidocrocite, $Fe(OH)_3$, ferrihydrite, jarosite, and Fe-oxyhydroxysulfate relative to the activity of Fe”; and gypsum.

X-ray diffraction and thermal analysis of sediment samples collected from abiotic zones within the treatment system suggested the presence of crystalline Fe oxyhydroxide minerals. such as hematite, lepidocrocite, goethite, and jarosite. Biotic wetland cell sediment characterizations suggested the presence of amorphous iron minerals such as ferrihydrite and $Fe(OH)_3$. Apparently high Fe^{3+} activity and low oxygen diffusion rates in the lower biotic subsurface environment inhibited the kinetics of crystalline iron precipitation. Instead, amorphous ferrihydrite appeared to dominate the wetland compost area. Some goethite, lepidocrocite, and hematite, however, were observed near the surface in wetland cells and were most likely attributable to increased oxygen levels from surface aeration and/or oxygen transport by plant roots.

A similar attempt was made to assess potential Al solubility control minerals in interstitial solution and surface water samples using the stability diagram (Fig. 7). Mineral phases examined included gibbsite ($Al(OH)_3$), alunite, jurbanite, and basuluminite with associated log K values of -33.95, -85.4, -17.2, and -1 17.5. respectively.” Points on the diagram are separated into two major clusters, one that is undersaturated with respect to gibbsite and another which is supersaturated. The point at which the jurbanite solubility line crosses that of gibbsite occurs at a pH of ≈4.5,[45] and is the pH value that differentiates the two clusters A possible solubility control sequence for solution samples with pH values below 4.5 include alunite and jurbanite. Although alunite has been shown to be the more stable mineral at pH ≤ 4.5,[20] the solubility of jurbanite is more sensitive to SO,” activity and may be more consistent with species found in this system.

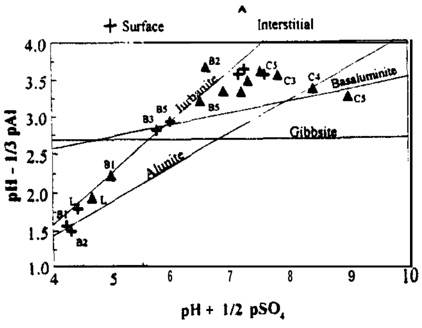

Figure 7. Mineral stability diagram depicting solubility lines of jurbanite, basaluminite, gibbsite, and alunite.

A possible solubility controlling sequence for solution samples with pH > 4.5 includes jurbanite and basaluminite for water samples in aerobic zones; and alunite, basaluminite and gibbsite in anaerobic zones. The interstitial solution from wetland cell #5, which displays the lowest concentration of sulfate and highest pH, is undersaturated with respect to all aluminum sulfate minerals. Apparently, the production of alkalinity and reduction of sulfate associated with progressive stages of treatment in the wetland due to gypsum precipitation is correlated with a shift in the solubility control from jurbanite to basaluminite or alunite. In solutions above pH 4.5 and low pSO_4^{2-} conditions, the precipitation of jurbanite is possible however, jurbanite is thermodynamically less stable than basaluminite which itself is less stable than alunite.” Thus, solubility control may eventually transfer to the more stable mineral (alunite) as the system ages.

Elevated pH and pCO_2 levels in anaerobic zones of the wetland due to carbonate dissolution may contribute to Mn and Fe retention. Using the MINTEQA2 speciation program, solution saturation indices (logQ/K), where Q = ion activity product and K = solubility product constant, were calculated to determine possible precipitation of metal carbonates in the system. A pCO_2 value of 0.3, representative of flooded soils’ was used to determine the solubiiity of rhodochrocite ($MnCO_3$) in the wetland substrate. Using pH values from interstitial solutions and the reaction:

$$MnCO_{3(s)} + 2H^+ \leftrightarrow Mn'' + CO_{2(g)} + H_2O, \text{ where } \log K = 8.08,^{44}$$

the log Q was found to be 8.45. This results in a saturation index (Q/K) of 1.04, which represents a state of near equilibrium. Thus, elevated substrate Mn concentrations may be attributed to precipitation of rhodocrocite.

A similar procedure was performed to determine the stability of siderite ($FeCO_3$) in the wetland substrate. Using a pCO_2 of 0.3, pH values from interstitial solutions and the reaction:

$$FeCO_{3(s)} + 2H^+ \leftrightarrow Fe^{2+} + CO_{2(g)} + H_2O, \text{ where } \log K = 7.92,'$$

the log Q was calculated to be 9.68, and the saturation index (Q/K) 1.22. Therefore, the solution conditions are also favorable for siderite precipitation. Evidently, the precipitation of metal carbonates in the substrate zones are facilitated by high pCO_2 rates that occur in flooded environments.

The retention of Fe and Mn carbonates in the substrate benefits the AMD treatment process, but negative implications could result if these reactions occur within the anoxic limestone drains. The formation of rhodocrocite and siderite may reduce ALD performance by decreasing the reactivity and permeability of the limestone bed.’ As with the limestone substrate, pCO_2 values in ALD are generally high. Using the equilibrium reactions described earlier, the solubility of $FeCO_3$ and $MnCO_3$ was tested in the lagoon, first precipitation basin and first wetland cell for interstitial and surface waters In all cases, the solutions were undersaturated with respect to the minerals, suggesting that precipitation is not occurring. However, manipulation of the data revealed that precipitation could occur if the pH inside the ALD exceeds 6.0 Current inlet/outlet water quality prohibits Mn or Fe carbonate precipitation within the drains but a decrease in the ALD flow rate could increase retention and expedite limestone dissolution, thus raising pH to levels sufficient for metal carbonate precipitation.

5. SUMMARY AND CONCLUSIONS

This study represents an attempt to revive a failed constructed wetland treating one of the most toxic AMD’s, in terms of Fe and acidity, that could be encountered. Two years after renovation the treatment efficiency data are very encouraging. The modified SAPS design appears to be functioning as predicted during the post renovation period. Results reveal that limestone dissolution and sulfate reduction in the substrate are producing an adequate amount of alkalinity to raise pH levels for sufficient precipitation of metal carbonates in reduced zones and metal hydroxides in oxidized zones. Samples of limestone gravel extracted form the substrate showed no evidence of armoring and solution sample analyses confirmed that anoxic conditions persisted in the subsurface zones

The dissolution of limestone within the wetland system contributed to the generation of alkalinity and neutralization of ≈42 metric tons of acidity Per year. An estimation of the system’s longevity is difficult to determine based upon exhaustion of the organic compost because many factors contribute to its saturation.[34] However, a budget estimate of the acidity consumed by limestone dissolution suggests that under the existing conditions, limestone would need to be replaced in the wetland substrate and in the ALD’s after six years of operation. The renovation of the Jones Branch wetland cost ≈$60,000. If current conditions persist, the system will precipitate nearly 90 metric tons of iron and treat 252 metric tons of acidity in six years The estimated cost per ton of acid neutralization is $227 over the six-year period. This cost is from 7% ($Ca(OH)_2$) to 92% (NaOH) lower than estimates for conventional treatment with caustic materials

The precipitation and/or retention of minerals in the AMD constructed wetland treatment system is a complex process with no single dominating control sequence. Rather, multiple reactions and interactions occur simultaneously at the surface and within the substrate creating a mixed composition of soluble and insoluble species Crystalline minerals such as hematite, lepidocrocite, goethite and jarosite appear to control Fe chemistry in aerobic zones, such as the lagoon and precipitation basins where SO_4/Fe ratios are low. At high SO_4/Fe ratios, jarosite is transformed to other Fe-oxyhydroxysulfate and goethite formation is inhibited. In wetland cell substrates, the control of Fe chemistry is transferred to amorphous iron minerals, such as ferrihydrite and $Fe(OH)_3$. Aluminum speciations in the treatment system suggest jurbanite, alunite, and basaluminite as mineral controls of soluble Al. In surface waters and abiotic substrates aluminum solubility is controlled by alunite at low pH (<4.5) levels and jurbanite at higher pH (>4.5) regions. Solubility in biotic zones appears to be controlled by jurbanite and basaluminite

The results also indicated that limestone dissolution and alkalinity production play a major role in the mineral formation process and long term operational efficiency of the system. The formation of gypsum and rhodochrocite and possibly siderite as by-products of limestone dissolution may have an impact on S, Mn. and Fe solubility controls, In addition, high metal (Fe. Al, Mn) retention levels observed in the treatment system are directly related to increased pH conditions. As long as pH conditions remain constant, continued treatment is expected, however, armoring, clogging, or complete dissolution of the limestone gravel could result in decreased buffering capacity, resolubilization of metals and potential reprecipitation of pyrite. Thus, the need for future monitoring and maintenance of this high alkalinity producing system is both evident and essential.

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